AN INVESTIGATION OF CAPILLARY SPREADING POWER OF EMULSIONS

Crosland

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AN INVESTIGATION OF CAPILLARY SPREADING POWER OF EMULSIONS

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AN INVESTIGATION OF CAPILLARY SPREADING POWER OF EMULSIONS

CHAPTER I

INTRODUCTION AND SCOPE OF THE PROBLEM

The penetration of porous materials by fluids is especially important to the manufacturer of textiles, papers, and leathers. While some work has been done on the flow of pure liquids in capillary spaces, little consideration has been given to the penetration of emulsions in small capillaries. As emulsions have steadily become more important in these industries there is a growing need for adequate information on their capillary spreading or penetrating properties.

This paper is a study of the influence of the viscosity-surface tension ratio on the penetration of an emulsion in a horizontal capillary. The capillary spreading power is defined as the time necessary to penetrate a fixed distance under the influence of capillary forces and as will be shown, is proportional to the viscosity-surface tension ratio.

The validity of equations which had been developed by Washburn[1] and Rideal[2] for the flow of pure liquids into cylindrical capillaries

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[1] E. W. Washburn, "The Dynamics of Capillary Flow", Physical Review, 17:276, 1921.

[2] Eric K. Rideal, An Introduction to Surface Chemistry (London: Cambridge University Press, 1930), p. 44.

was investigated for emulsions and certain modifications were necessary to describe the flow.

The results are applicable to the spreading of an emulsion in a porous material such as spun yarn or paper where capillary forces predominate. It was not intended to cover complete consideration of wetting phenomena or the spreading of emulsions independent of capillary forces. From the standpoint of application the absolute rate of penetration of an emulsion for a specific porous material is of little value because of the difficulty in obtaining identical test samples, therefore an effort was made to establish the factors or properties involved for maximum or minimum emulsion penetration.

The remaining portion of this thesis is divided into chapters for clarity. Chapter II contains a brief review of previous investigations of capillary flow, wetting, spreading, and penetration. There is presented a description of all equipment in Chapter III and in Chapter IV a discussion of the stability, type, and physical properties of the emulsion investigated. Chapter V shows the treatment of the findings of this investigation and the functions involved in capillary spreading. The conclusions and the application of results are discussed in the final chapter.

CHAPTER II

REVIEW OF THE LITERATURE

Many papers have been published on capillary flow of liquids, though few could be found covering the horizontal flow of liquids under capillary pressure. Volumes of literature have been published on surface tension and much has been written in regard to wetting, spreading, and penetration of solids by liquids. Pure liquids, mixtures, and colloids have received a great deal of attention; emulsions, however, are hardly mentioned in connection with any observations other than surface tensions.

I. CAPILLARY FLOW

In 1906 Bell and Cameron[1] first deduced the relationship between the length of travel and the time of a liquid flowing along a horizontal capillary from a large reservoir under the influence of surface forces only as

$$\frac{x^2}{t} = \text{constant}$$

where x = distance

t = time.

Later in 1921 Washburn investigated horizontal capillary flow

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[1] J. M. Bell, and E. K. Cameron, "Flow of Liquids Through Capillary Spaces", Journal of Physical Chemistry, 10:659, 1906.

assuming the validity of Poiseuille's Law and found[2]

$$x^2 = \frac{\sigma \cos\theta}{2\mu} rt$$

where x = distance in centimeters

σ = surface tension in dynes/cm.

θ = angle of contact of liquid with surface

μ = viscosity in poises

r = radius of capillary in centimeters

t = time in seconds.

In 1922 Rideal obtained the following expression for the flow of a wetting liquid[3]

$$t = \frac{2\mu}{\sigma r} x^2 - \frac{\rho r^2}{8\mu} \log x + \frac{\rho^2 r^6}{32\mu^3 x^2}$$

where ρ = density in gms./c.c.

x = distance in centimeters

σ = surface tension in dynes/cm.

θ = angle of contact

μ = viscosity in poises

r = radius of capillary in centimeters

t = time in seconds.

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[2] E. W. Washburn, "The Dynamics of Capillary Flow", Physical Review, 17:276, 1921.

[3] Eric K. Rideal, "Flow of Liquids Under Capillary Pressure", Philosophical Magazine, 44:1152-9, 1922.

For small values of r this reduces to Washburn's form

$$x^2 = \frac{\sigma \cos\theta}{2\mu} rt.$$

As mentioned before, this work was done on pure liquids; it is the intention of the writer to determine if this relationship holds for an emulsion of small particle size.

II. SURFACE TENSION

According to Freundlich, "there are few physical quantities for which so many methods of measurement exist as for surface tension at the interface gas-liquid".[4] A survey of the literature shows numerous methods of determining surface tension and three excellent reviews are mentioned here.

Dorsey discusses in detail seventeen different methods of measurement including criticisms of each and a very complete bibliography.[5] Adam presents a fine summary and criticism of various methods of measuring surface tension.[6] Ferguson in a very thorough paper reviews twenty different procedures to determine surface tension of liquids.[7]

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[4] Herbert Freundlich, Colloid and Capillary Chemistry (London: Methuen and Company, Ltd., 1922), p. 12.

[5] N. E. Dorsey, "Measurement of Surface Tension", Scientific Papers of the Bureau of Standards, 21, Bulletin No. 540, 575-95, 1926.

[6] Neil K. Adam, The Physics and Chemistry of Surfaces (Oxford: Clarendon Press, 1930), p. 293-324.

[7] Allan Ferguson, Science Progress, 9: 428, 1914-15.

III. WETTINGS, SPREADING, AND PENETRATION

A detailed discussion of the theory of wetting and wetting phenomena can be found in such publications as those of Bartell and Osterhoff,[8] and of Adam.[9] The wetting and spreading of liquids is reviewed by Burdon[10] and the Report of the Leather Trades' Chemists.[11]

Capillarity and penetration is discussed at length by Freundlich,[12] and a very comprehensive treatise on the penetration of paper by liquids was published in the Paper Trade Journal.[13]

Since the theories of wetting, spreading, and penetration are complex and incomplete for pure liquids, little attention has been given to emulsions. It is beyond the scope of this paper to cover the validity of these theories for emulsions; however, they are so closely related to this study that they should be included in this literature survey.

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[8] F. E. Bartell, and H. J. Osterhoff, "Three Fundamental Types of Wetting", Journal of Physical Chemistry, 34:1399-1441, 1930.

[9] Adam, op. cit., pp. 167-227.

[10] R. S. Burdon, *Surface Tension and Spreading of Liquids* (London: Cambridge University Press, 1940), pp. 1-85.

[11] Wetting and Detergency, Report of the International Society of Leather Trades' Chemists, (New York: Chemical Publishing Company of New York, Inc., 1930), pp. 1-208.

[12] Freundlich, op. cit., pp. 5-233.

[13] Institute of Paper Chemistry, "Penetration of Papers by Liquids and Solutions", Paper Trade Journal, 110: No. 4, 44-40, 1940.

CHAPTER III

EQUIPMENT

Certain determinations were necessary to calculate the capillary spreading power of an emulsion and these included surface tension, viscosity, density, and time of capillary flow. Reasons for selection and descriptions of the apparatus are given on the following pages.

I. SELECTION

For surface tension measurements of emulsions the Du Nouy Precision Interfacial Tensiometer was used. This was selected because the instrument is well adapted for rapid and accurate measurement of the surface tension of colloids and is independent of the angle of contact.[1] As discussed by Du Nouy, surface active agents and colloids tend to become adsorbed or concentrated at the surface causing a drop in surface tension as function of time, because adsorption is not instantaneous. Therefore, any static or equilibrium method of measurement is subject to this error.

To measure the viscosity a Saybolt Universal Viscosimeter with automatic temperature control was used, and the density of the emulsion was determined by a hydrometer calibrated to the fourth decimal place. All pH determinations were made with a Beckman, Model H-2, pH meter.

For capillary flow a horizontal capillary tube attached to a large

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[1] P. Lecomte Du Nouy, Surface Equilibria of Colloids (New York: The chemical Catalog Company, Inc., 1926), p. 21.

reservoir was used. This apparatus was designed for simplicity and for ease of cleaning and operation.

II. DESCRIPTION AND OPERATION

Equipment with the exception of the horizontal capillary is standard and a description is unnecessary. The accuracy of the Saybolt Universal Viscometer[1] and the Interfacial Tensiometer[2] is within one per cent.

The dimensions of the horizontal capillaries can be seen in Figure 1. The diameters of the capillaries were determined by filling the tubes with mercury and calculating the average size from the weight of mercury.

In measuring the time of flow capillaries were first cleaned, and then flushed with the liquid under investigation several times to insure complete wetting of the tube and a zero angle of contact. On standing for long periods of time exposed to air the oil phase tends to preferentially wet the capillary surface; therefore, readings were taken immediately following wetting of the tube. Prior to measurements several c.c. were allowed to flow through the capillary. Then the apparatus was placed in a vertical position and the liquid returned to the reservoir. Finally the tube was placed in a horizontal position and the time of flow recorded for twenty and forty centimeters. The height of the liquid above the capillary was 0.25 centimeters and remained practi-

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[1] Sophia Berkman, and Gustav-Egloff, Emulsions and Foams (New York: Reinhold Publishing Corporation, 1941), p. 506.

[2] Adam, op. cit., p. 320.

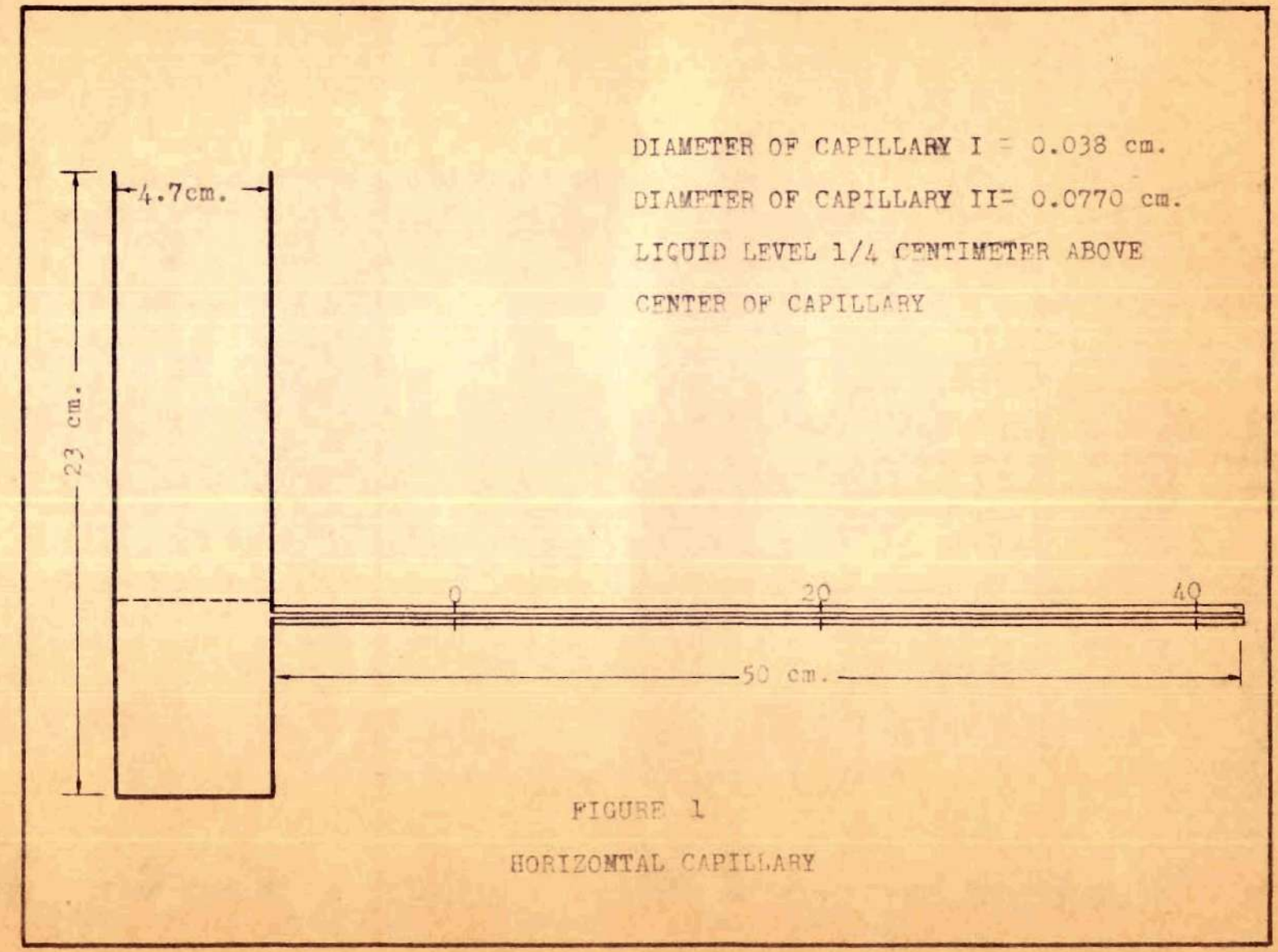

FIGURE 1

HORIZONTAL CAPILLARY

cally constant during measurements. The effect of this head on capillary flow is less than 1 per cent (Appendix, p.39).

CHAPTER IV

SELECTION, STABILITY, AND PHYSICAL PROPERTIES OF EMULSIONS

A great deal of time was consumed in formulating an emulsion which had a low viscosity and high stability over long periods of time. It was also considered desirable to obtain a minimum uniform particle size in the internal or oil phase so that reproduceable capillary and surface tension measurements could be established.

The type of emulsion selected for these measurements was an oil in water, non-ionic emulsion containing 20 per cent refined white mineral oil as the internal phase. Sorbitan Monopalmitate and a Polyoxyalkylene Derivative of Sorbitan Monopalmitate were used as non-ionic emulsifiers, each at a concentration of 2.2 per cent. Pentachlorophenol (0.1 per cent) and the Sodium Salt of Pentachlorophenol (0.1 per cent) were used as preservatives and the remaining 75.4 per cent was distilled water.

Non-ionic emulsifiers of the ester type were selected because of their stability to electrolytes, relative chemical inertness, and the extremely fine particle size (less than one micron) of the resulting mineral oil emulsion.[1]

The phenol compounds were added to the emulsion as preservatives when it was found that the original white mineral oil emulsion supported mold growth at the air liquid interface after several weeks in a closed container.

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[1] Atlas Powder Company, "Surface Active Agents", p. 1-13, 1945

To attain a minimum uniform particle size the emulsion was homogenized three times at a pressure of 3500 pounds per square inch through a commercial two stage homogenizer of 400 gallons per hour capacity.

PHYSICAL PROPERTIES

Determinations of the surface tension, viscosity, pH, and density were made each week during the entire test period of eight weeks and no significant changes in physical properties were observed (Table I). Slight deviations occuring in this table are considered well within the experimental error of the equipment used.

Microscopic examination at 440X and at 950X (oil immersion) revealed no apparent change in particle size by comparison of slides. Though no actual size frequency analysis was made, microscopic observations excluded appreciable increase in the particle size of the emulsion during the test period.

Extreme care was exercised in minimizing the emulsion's exposure to air, as evaporation of the external or water phase causes film formation or a high concentration of emulsifier and oil at the surface. Samples were kept in sealed jars as full as possible and remained undisturbed until measurements were made. It was observed that vigorous shaking and stirring of this emulsion at temperatures as low as nine degrees Centigrade produced an increase in viscosity; therefore, all unnecessary agitation was eliminated.

The effect of temperature on the surface tension and viscosity of this 20 per cent emulsion was observed and the results are shown in Figures 2, and 3. In Figure 2 the surface tension decreases almost

TABLE I

PHYSICAL PROPERTIES
OF TEST EMULSION

Time in weeks	Surface Tension in dynes/cm	Viscosity in centipoises	pH	Density in gm./cc.	Temp. °C
1	33.6	2.81	7.7	0.960	28
2	33.4	2.82	7.7	0.960	28
3	33.5	2.81	7.7	0.960	28
4	33.6	2.81	7.8	0.960	27*
5	33.6	2.82	7.7	0.960	28
6	33.8	2.80	7.7	0.960	27*
7	33.6	2.81	7.7	0.960	28
8	33.6	2.81	7.7	0.960	28

*Physical properties corrected to 28° C.

linearly as the temperature increases. In Figure 3 the viscosity decreases with increasing temperature at a very rapid rate from nine to twenty degrees Centigrade; however, from twenty to forty degrees the rate is considerably less.

Emulsion concentration, per cent oil, was plotted against surface tension in Figure 4, and against viscosity in Figure 5 at twenty nine degrees Centigrade. As the concentration increases the rate of drop in the surface tension decreases when the concentration approaches 20 per cent. In Figure 5 the viscosity increases with an increasing rate as the concentration approaches 20 per cent.

The effect of temperature and concentration on the emulsion density can be seen in the Appendix, pages 43 and 44, Figures 10 and 11. It will be observed from Figure 10 that density is not a linear function of temperature and that in Figure 11 density is a linear function of concentration.

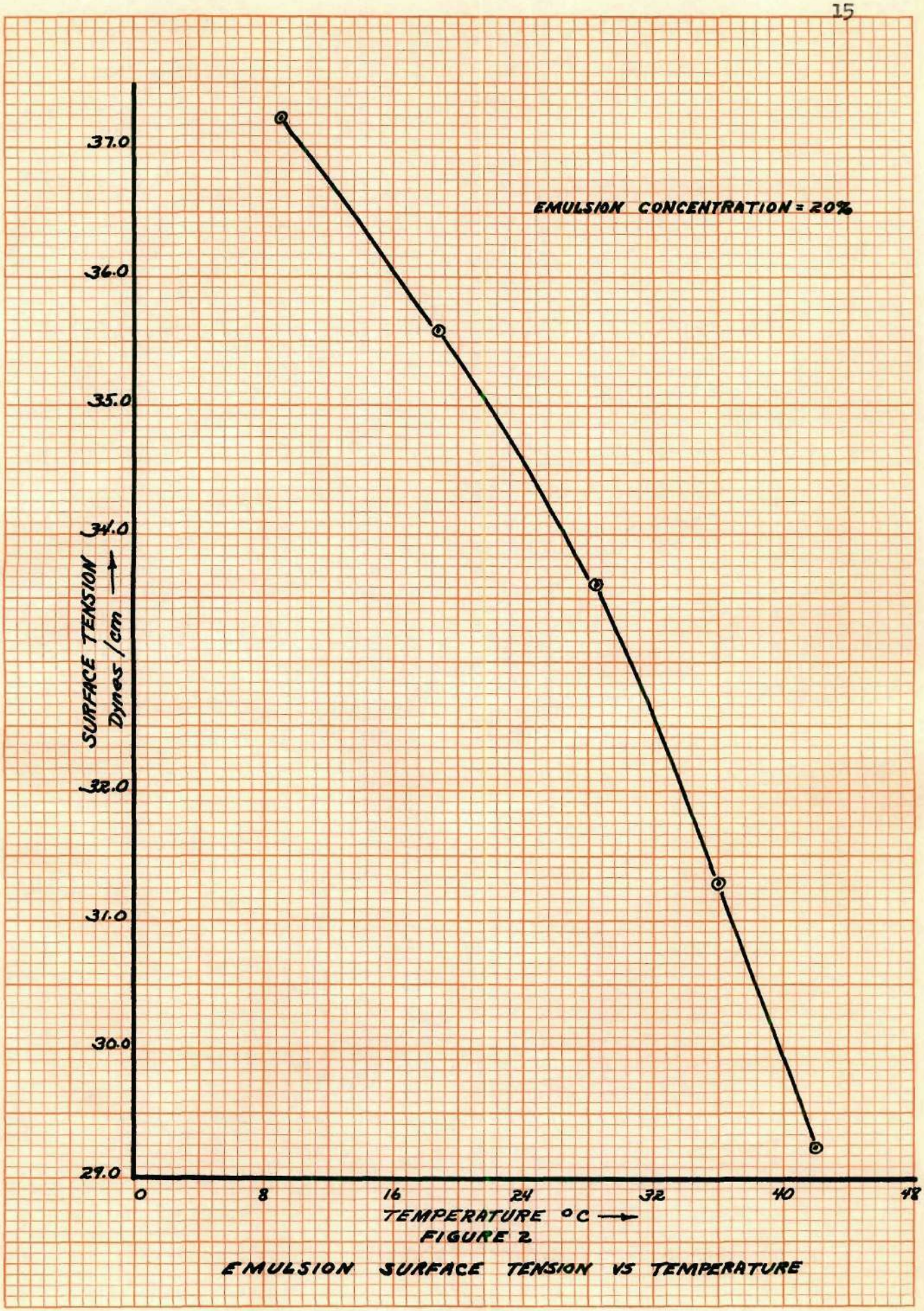

FIGURE 2

EMULSION SURFACE TENSION VS TEMPERATURE

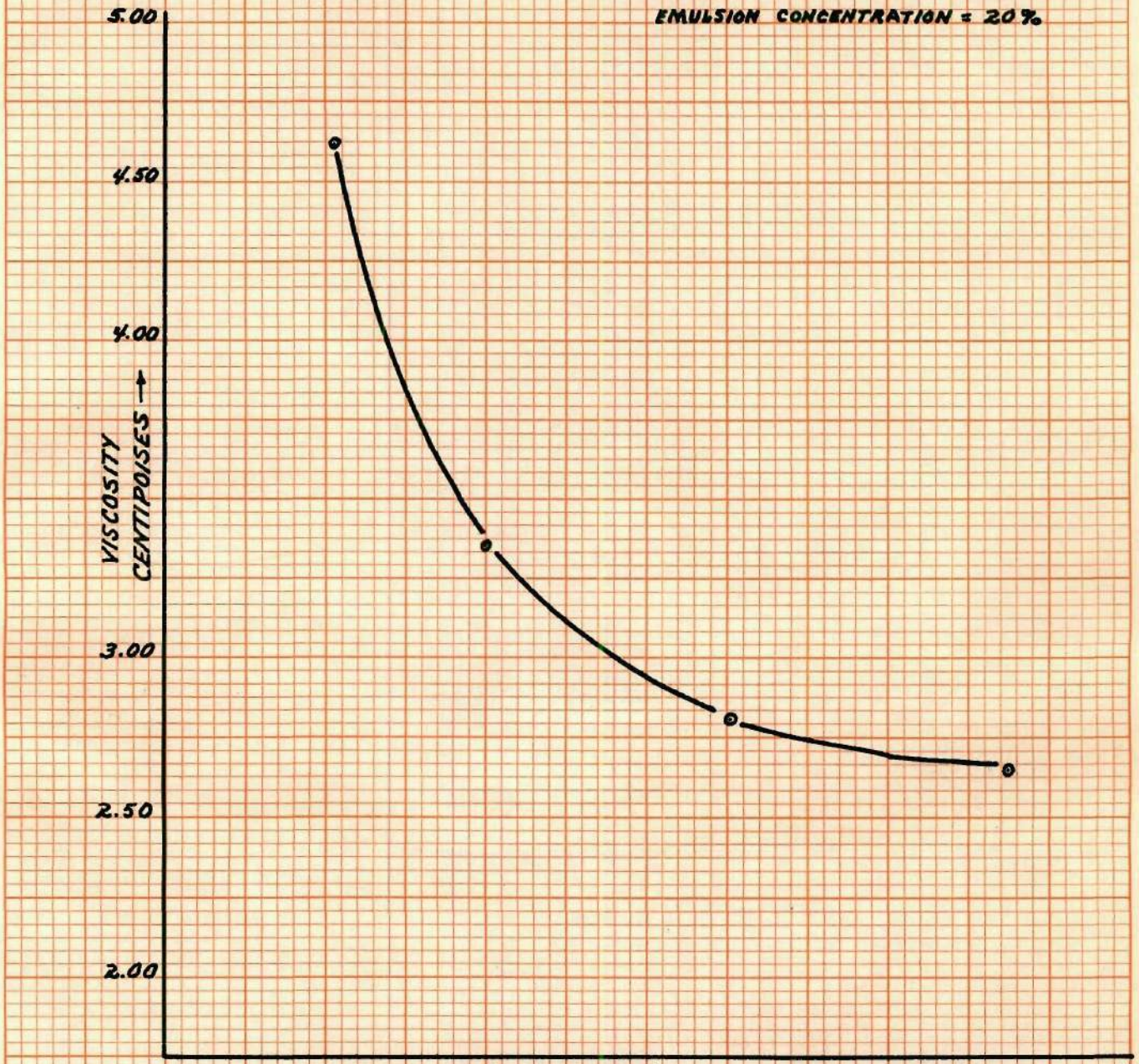

FIGURE 3

EMULSION VISCOSITY VS TEMPERATURE

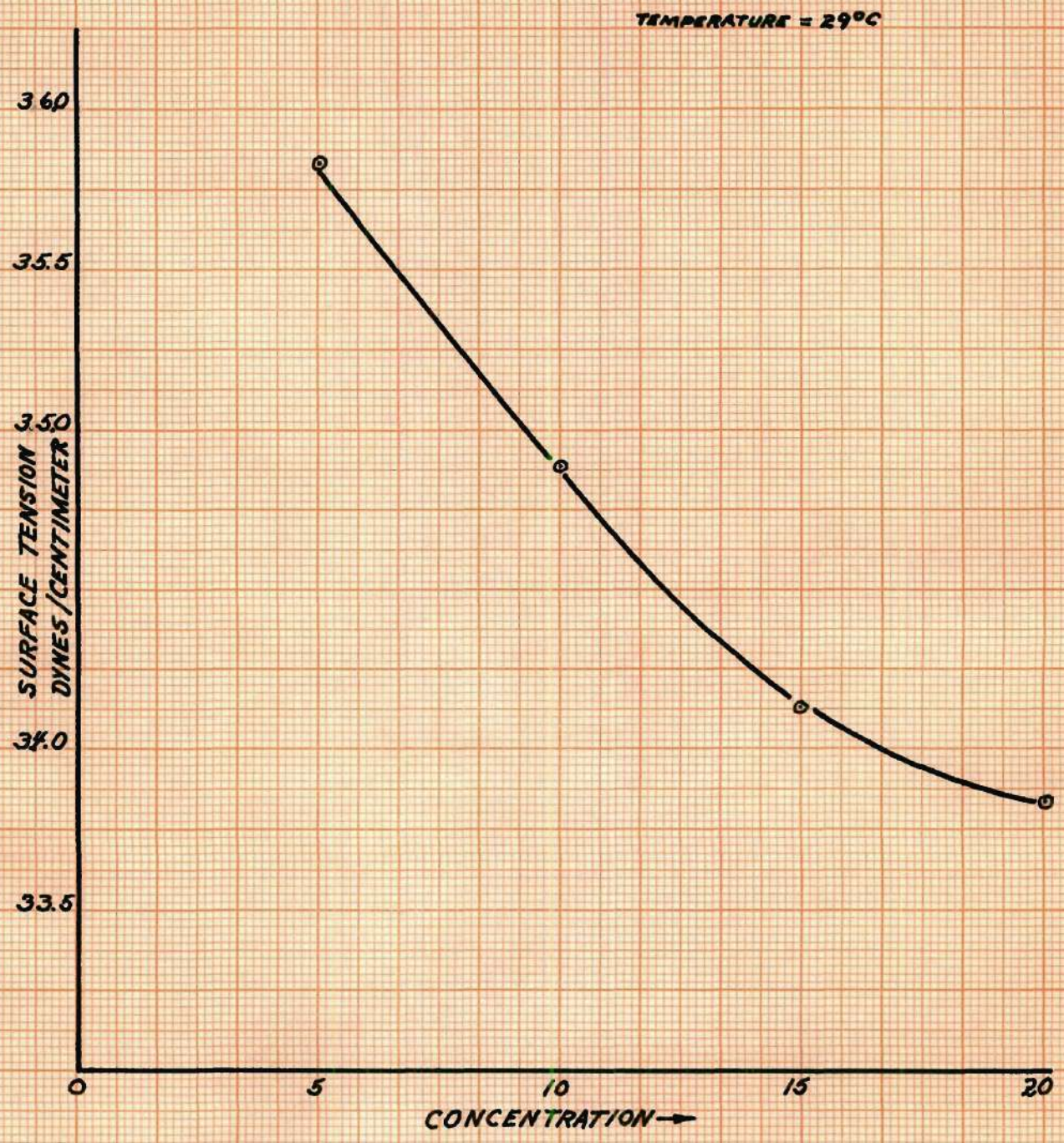

FIGURE 4

EMULSION SURFACE TENSION VS CONCENTRATION

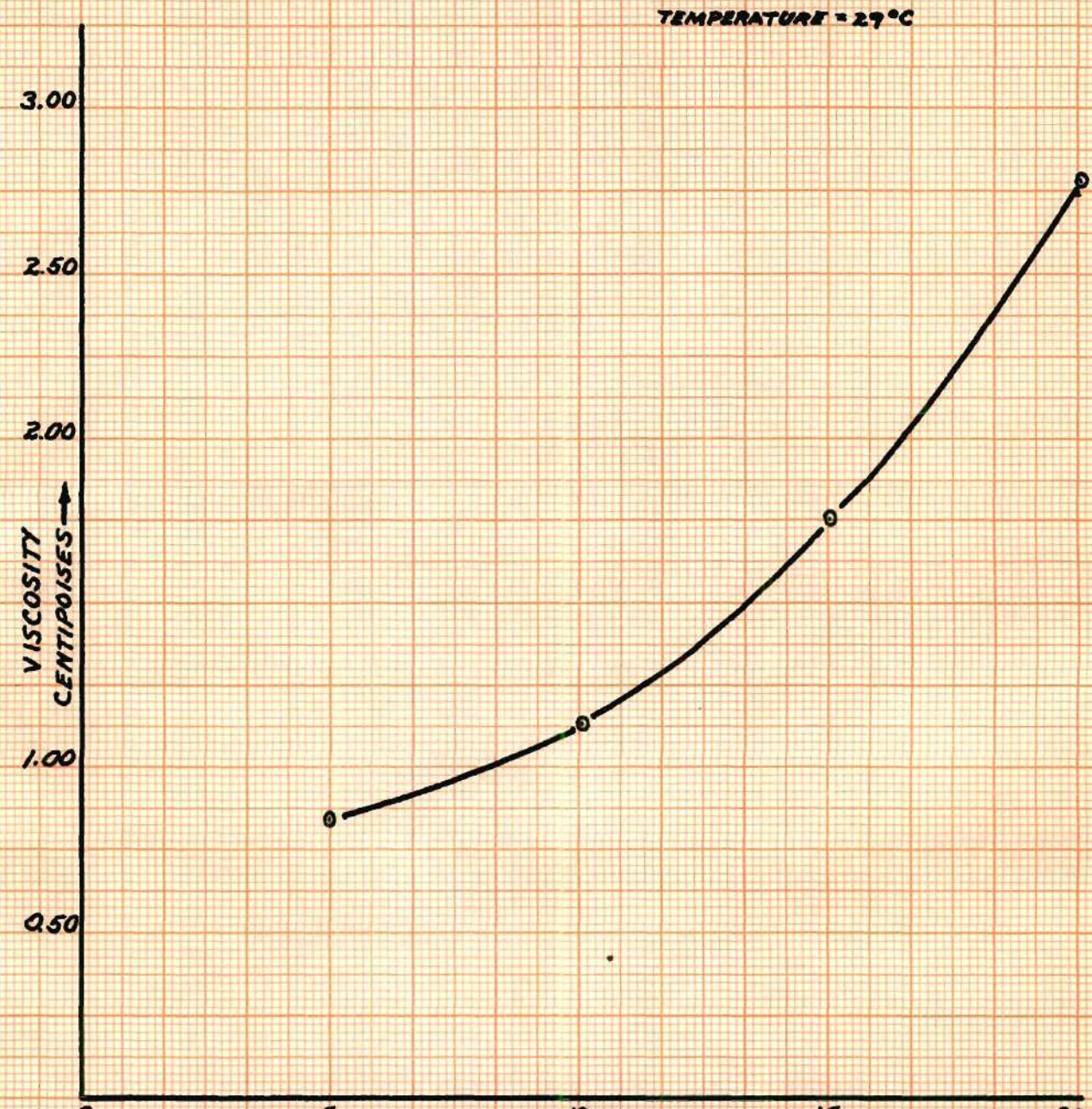

FIGURE 5

EMULSION VISCOSITY VS CONCENTRATION

CHAPTER V

CAPILLARY SPREADING POWER

The first section of this chapter deals with the development of equations for the time of flow of an emulsion in a horizontal capillary. The later sections cover the influence of certain variables on the penetration time.

I. DEVELOPMENT OF EQUATIONS

In the following sections $\underline{X}$ will be used to denote the distance in centimeters traveled by the emulsion in a horizontal capillary, $\underline{\sigma}$ the surface tension in dynes per centimeter, $\underline{\mu}$ the viscosity in poises, $\underline{t}$ the time in seconds, $\underline{\rho}$ the density in grams per cubic centimeter, $\underline{r}$ the radius in centimeters, and $\underline{\theta}$ the angle of contact of the emulsion with the solid surface.

Beginning with the equation developed by Rideal[1]

$$(1)\quad t = \frac{2\mu}{\sigma r \cos\theta} X^2 - \frac{r^2 \rho}{8\mu} \log X + \frac{\rho^2 r^5}{512\mu^3 X^2}$$

it was found (Appendix, p.38) for values of the radius of 0.0354 centimeters and less that the last two terms on the right hand side were negligible and the equation reduces to

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[1] Rideal, loc. cit.

$$(2)\quad t = \frac{2X^2}{r\cos\theta}\,\frac{\mu}{\sigma}\ .$$

Since the distance X in these tests was fixed at either twenty or forty centimeters, the radius was constant at 0.0354 or 0.0190 centimeters, and the capillary was wetted several times with the emulsion to obtain a zero angle of contact, this equation reduces to

$$(3)\quad t = K\,\frac{\mu}{\sigma} \quad \text{and} \quad K = \frac{2X^2}{r}\ .$$

The values for the surface tension and viscosity were determined by independent observations and were shown in Figures 2, 3, and 4 of Chapter IV. The ratio of viscosity to surface tension and the observed penetration time for 20 centimeters of horizontal capillary under varying conditions of concentration, temperature, and capillary radius can be seen in Table II.

It was readily seen in equation (3) that the μ/σ ratio plotted against the penetration time should give a straight line of slope $\frac{1}{K}$. This was found to be true, and Figures 6 and 7 show the results of μ/σ versus time for capillary tubes of radii 0.0354 and 0.019 centimeters respectively.

The slope of the line was easily determined from Figures 6 and 7 and K was found to be 6.58×10^4 for radius 0.354 cm. and 9.02×10^4 for radius 0.0190 cm. (Appendix, p. 39.

Equation (3) is now

$$(4)\quad t = 4.87 \times 10^4\,\mu/\sigma \text{ for radius } .0354$$

TABLE II

TIME OF CAPILLARY FLOW
VS.
VISCOSITY-SURFACE TENSION RATIO

Emulsion Concentration	Radius	Temperature °C	Penetration Time for 20 cm.	Observed $\eta/\sigma \times 10^{-4}$
5%	.0354	29.0	12.0	2.35
10%	.0354	29.0	16.1	3.23
15%	.0354	29.0	26.0	5.24
20%	.0354	29.0	40.4	8.19
20%	.0354	9.0	59.6	11.99
20%	.0354	16.0	46.2	9.51
20%	.0354	29.0	40.0	8.19
20%	.0354	32.8	42.0	8.47
20%	.0354	41.0	43.5	9.01
5%	.0190	29.0	22.4	2.35
10%	.0190	29.0	29.8	3.23
15%	.0190	29.0	48.4	5.24
20%	.0190	29.0	75.2	8.19
20%	.0190	9.0	113.0	11.99
20%	.0190	16.0	90.0	9.51
20%	.0190	31.0	77.0	8.40
20%	.0190	32.8	80.2	8.47
20%	.0190	41.0	82.0	9.01

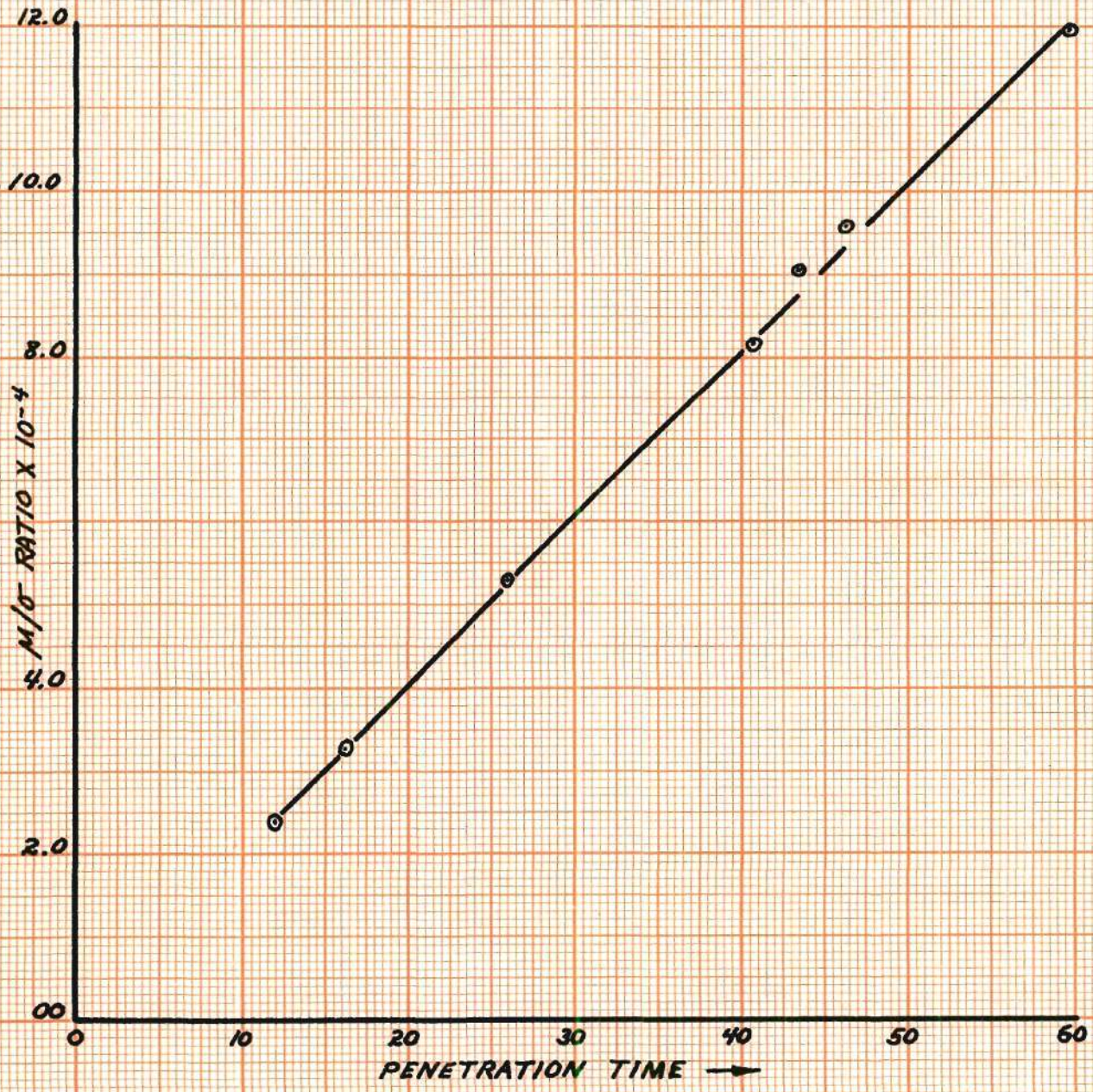

FIGURE 6

VISCOSITY - SURFACE TENSION RATIO VS PENETRATION TIME FOR RADIUS 0.0354 cm.

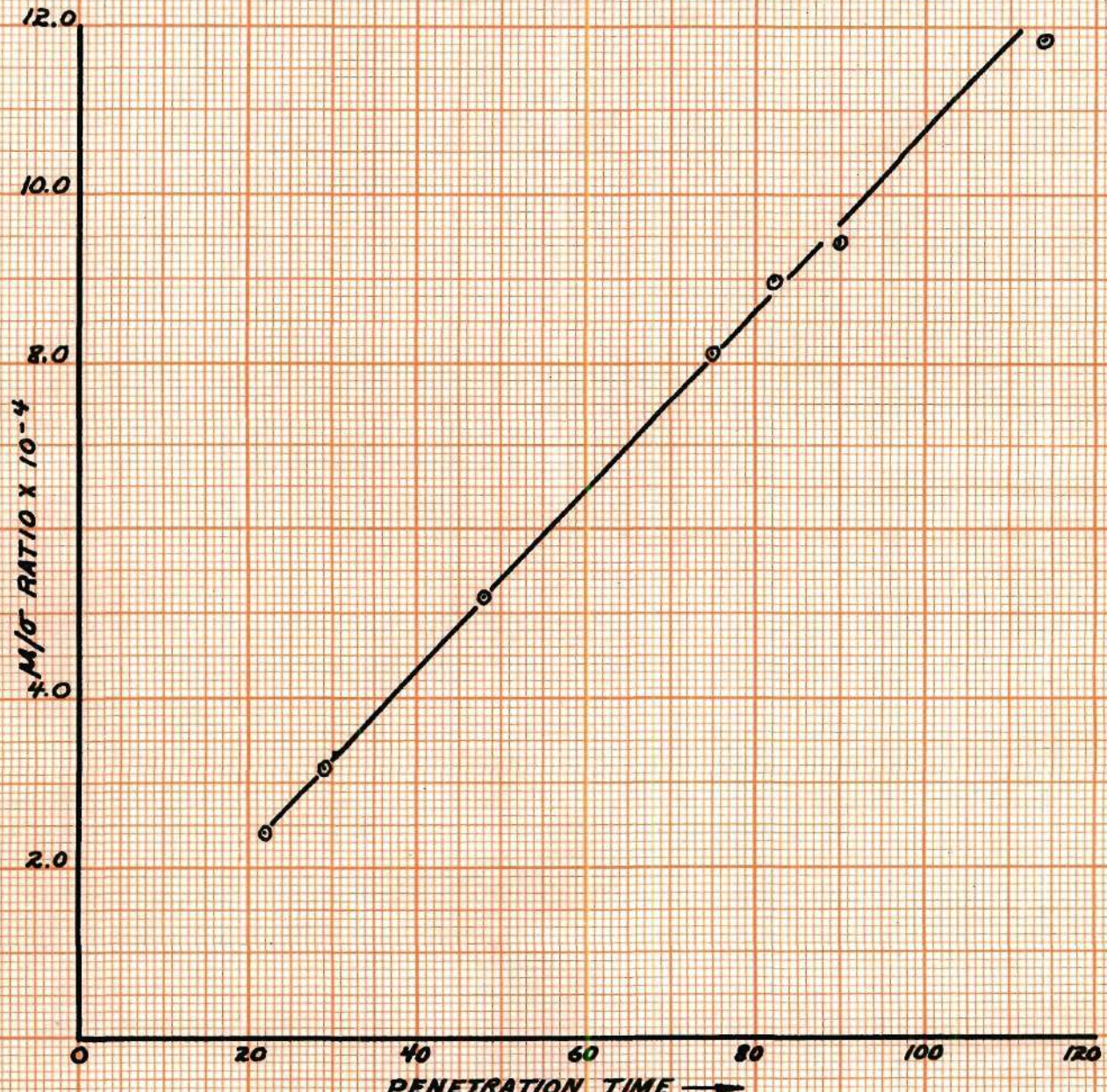

FIGURE 7

VISCOSITY – SURFACE TENSION RATIO VS PENETRATION TIME FOR RADIUS 0.0190 cm.

and

$$(5)\quad t = 9.05 \times 10^{4}\, \mu/\sigma \text{ for radius } .0190 .$$

If from equation (3) we substitute $\frac{2X^2}{r}$ for K to check the validity of equations (1) and (2) we find

$$(6)\quad 4.87 \times 10^{4} \neq \frac{2X^2}{r} \neq \frac{2(20)^2}{0.0354} \neq 2.26 \times 10^{4}$$

As it has been found experimentally[2] that

$$(7)\quad t = \frac{2X^N}{r\cos\theta}\,\mu/\sigma$$

sometimes fits the data better than equation (2), further consideration must be given to establish the power of $\underline{X}$.

From Table III (Appendix, p.40) the value of $\underline{t}$ at 20% concentration and twenty nine degree Centigrade for 20 cm. and 40 cm. penetration are substituted in the equation

$$t = \frac{2X^N}{r\cos\theta}\,\mu/\sigma$$

and assuming cos $= 1$

$$(8)\quad t_1 = \frac{2X_1^N}{r}\,\mu/\sigma$$

and

$$t_2 = \frac{2X_2^N}{r}\,\mu/\sigma \therefore \frac{t_1}{t_2} = \frac{X_1^N}{X_2^N}$$

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[2] Van den Akker, et. al., Paper Trade Journal, 109, No. 21, 279-88, November 23, 1939.

then

$$\frac{120.0}{40.4} = \frac{40^N}{20^N}$$

$$N = \frac{\log 2.980}{\log 2.000} = \frac{0.4742}{0.3010}$$

$$N = 1.575 .$$

Applying this value for the power of X to equation (6) for radius .0354 and radius .0190 we find

$$4.87 \times 10^{4} = K \frac{2X^{1.575}}{r}$$

then

$$K = \frac{4.87 \times 10^{4}}{1.758 \times 10^{4}} = 2.77 \text{ for radius .0354}$$

and

$$9.02 \times 10^{4} = K \frac{2\,X^{1.575}}{r}$$

then

$$K = \frac{9.02 \times 10^{4}}{3.27 \times 10^{4}} = 2.76 \text{ for radius .0190.}$$

Equation (2) becomes

$$(9)\quad t = \frac{2.77\,X^{1.575}}{r \cos\theta}\ \frac{\mu}{\sigma} \text{ for radius 0.0354 cm.}$$

$$(10)\quad t = \frac{2.76\,X^{1.575}}{r \cos\theta}\ \frac{\mu}{\sigma} \text{ for radius 0.0190 cm.}$$

Thus the general equation for the time of flow of this type of emulsion in a horizontal capillary under the influence of capillary forces alone is shown in equation (9) or (10).

II. EFFECT OF TEMPERATURE

The effect of temperature on the capillary spreading power or penetration time can be seen from the equation $t = K \frac{\mu}{\sigma}$ to vary as the viscosity-surface tension ratio varies with temperature. A plot of the viscosity surface tension ratio for a 20 per cent emulsion vs. temperature is given in Figure 8. The ratio μ/σ passes through a minimum around twenty nine degrees Centigrade and the penetration time is also a minimum at this point (Table II). The reason for this minimum can be seen in Figures 2 and 3 which show the rate of change of viscosity and surface tension with temperature.

III. EFFECT OF EMULSION CONCENTRATION

As would be expected the penetration time increases with increased percentage of oil in the internal phase. A plot of the viscosity-surface tension ratio at twenty nine degrees Centigrade vs. concentration is given in Figure (9). As the concentration increases the rate of increase in the viscosity-surface tension ratio becomes larger; the same applies to the time of penetration since t is proportional to $\frac{\mu}{\sigma}$.

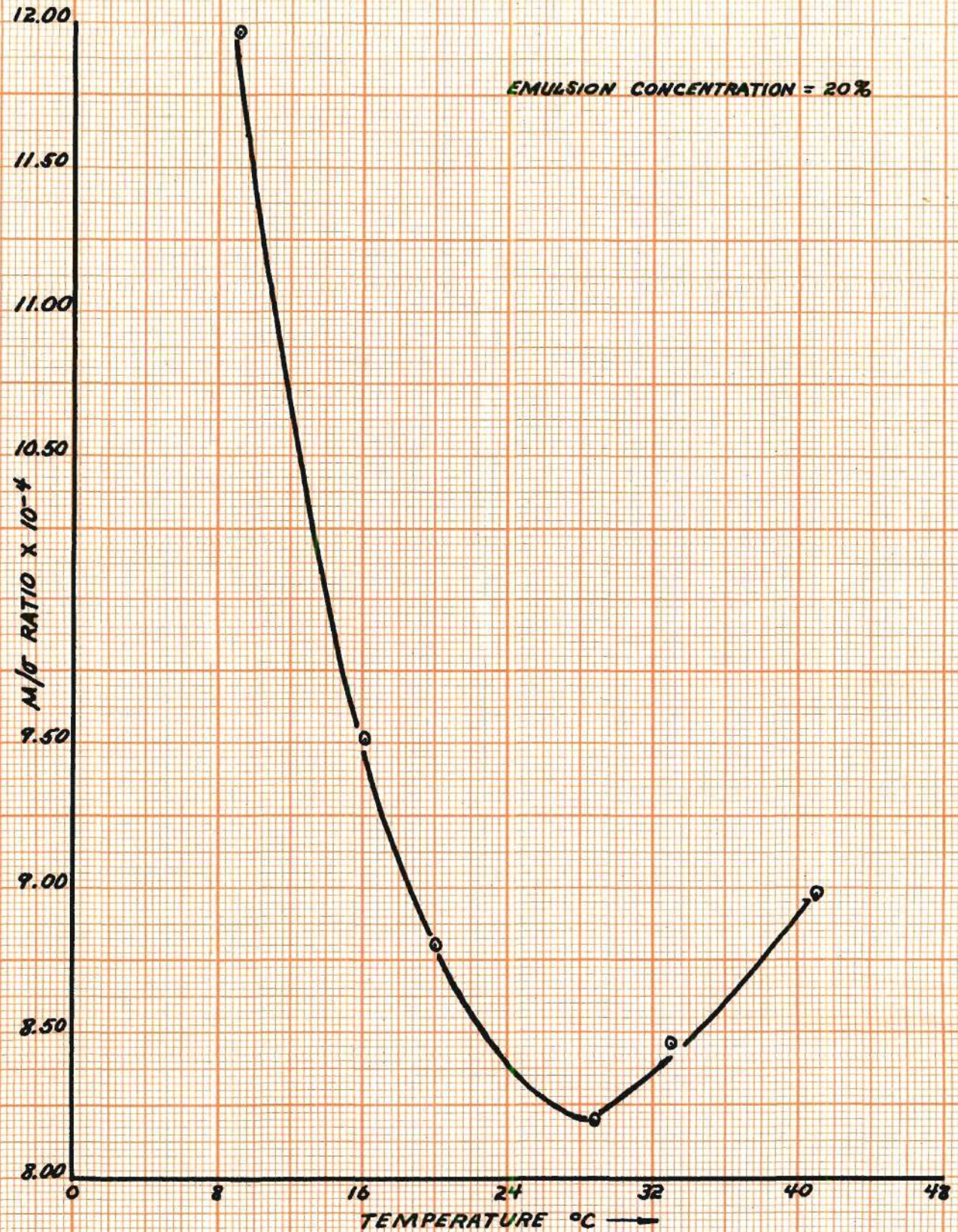

FIGURE 8

VISCOSITY-SURFACE TENSION RATIO VS TEMPERATURE

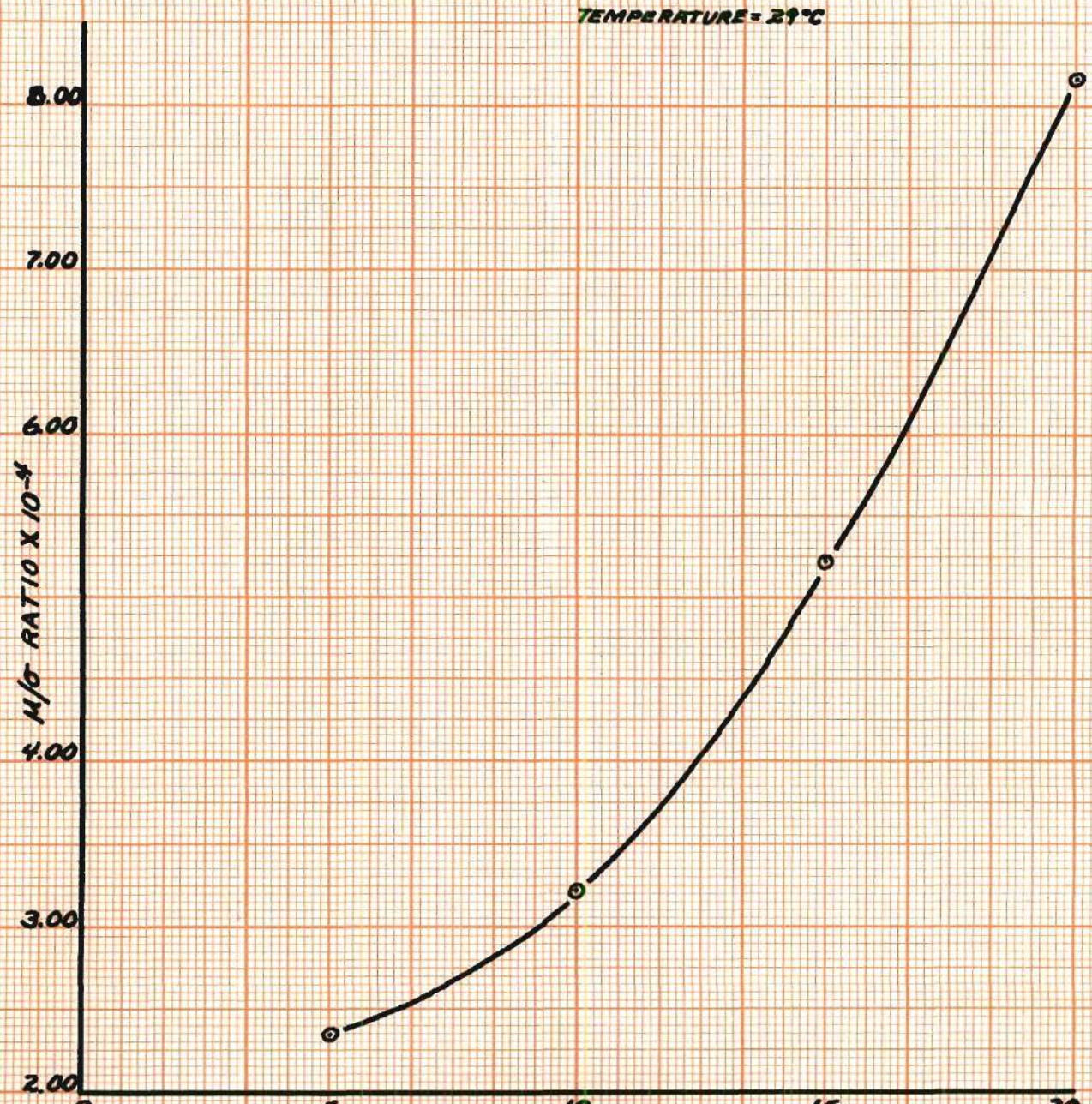

FIGURE 9

VISCOSITY – SURFACE TENSION RATIO VS CONCENTRATION

CHAPTER VI

This chapter summarizes the findings in the preceding chapters and the conclusions drawn from experimental work. The application of the findings of this study are briefly covered in the conclusions.

I. SUMMARY

This work is a study of the penetrating properties of an emulsion under the influence of capillary forces. It was intended to determine the effect of the viscosity-surface tension ratio on the penetration of an emulsion in a horizontal capillary. The time necessary to penetrate a fixed distance in a horizontal capillary was found to be proportional to the viscosity-surface tension ratio.

$$(1) \quad t = K \frac{\mu}{\sigma} .$$

This time was called the capillary spreading power of an emulsion. The capillary spreading power or penetration time of this type of emulsion was further found to be directly proportional to the 1.575 power of the distance traveled and inversely proportional to the radius of the capillary when the cos θ is equal to one or the angle of contact of the liquid with solid surface equals zero. Equation (2) shows this relationship.

$$(2) \quad t = 2.76 \frac{X^{1.575}}{r} \frac{\mu}{\sigma} .$$

The above equation describes the flow of an emulsion in a horizontal

capillary and is a modified form of Washburn's[1] equation

$$(3)\quad x^2 = \frac{2\sigma \cos\theta}{\mu} r t$$

for the flow of pure liquids in capillaries under the influence of capillary forces alone.

Experimental work involved the independent measurement of surface tension, viscosity, and time of horizontal capillary flow under varying conditions of temperature, emulsion concentration, capillary radius, and capillary length.

The emulsion used in these tests was a 20% refined white mineral oil emulsion with water as the external phase.

The behavior of this emulsion differs from that of water as the viscosity surface tension ratio passes through a minimum as the temperature is varied. This ratio for water is practically linear when plotted against the temperature.

II. CONCLUSIONS

From the preceeding section the capillary spreading power or penetrating time was given by equations (1) and (2). In applying these equations quantitatively to the penetration of any porous material we must consider a number of other factors. The angle of contact between the liquid and the porous material may not be zero. The pores of paper and yarn are generally not cylindrical. The length of the capillaries are very short and therefore the speed of flow may be very large. The

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[1] Washburn, loc. cit.

end effects due to such short capillary lengths may become appreciable. External pressure or surface forces may predominate over capillary forces. Finally, the emulsion may show an erratic behavior due to the filtering-out or adsorption of the dispersed or internal phase at or near the surface of the porous material. However, it it not possible to combine in one test the many variables involved and the advantage of applying capillary theories lies in the ability to determine accurately some of the variables which influence the rate of penetration.

In order to make equation (2) more general in form the power of X may be allowed to vary and the cos θ can be replaced. This equation becomes

$$(3) \quad t = K \frac{X^N}{r \cos\theta} \frac{\mu}{\sigma} .$$

From this equation the behavior of the fluid is measured by the viscosity surface tension ratio and that of the porous material by $1/r \cos\theta$. Since the properties of the porous material in practice are more difficult to control than those of the penetrating fluid, they have been considered only in their effect on the penetration time. Calculation of the radii of capillaries by this equation might be of interest, but pure liquids and not emulsions are much more practical for this consideration.

It is of greater interest here to establish the factors involved in maximum and minimum emulsion penetration of a porous material under capillary forces alone than to determine a quantitative relationship for the flow of an emulsion in a specific porous material. Examining equation (3) in this light reveals that for maximum emulsion penetration

or minimum penetration time the viscosity should be as low as possible, the surface tension high, the angle of contact small, the radius or equivalent radius large, and the capillary distance small. The penetration time is dependent on temperature as the viscosity-surface tension ratio varies with the temperature.

The capillary spreading power or penetration time of an emulsion in a horizontal capillary can be used as a relative measure of the penetration in a porous material under the influence of capillary forces alone, if the angle of contact of the emulsion with the solid is known or small in value; however, it can not be used as an absolute value of the penetration.

BIBLIOGRAPHY

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Adam, Neil Kensington, The Physics and Chemistry of Surfaces. London: Oxford University Press, 1930. 332 pp.

Akker, Van den, et. al., Paper Trade Journal, 109, No. 21, 279-88, November 23, 1939.

Atlas Powder Company, Surface Active Agents, Wilmington, Delaware, 1945. 17 pp.

Bartell, F. E., and Osterhoff, H. J., "Three Fundamental Types of Wetting", The Journal of Physical Chemistry, 34: 1399-1411, 1930.

Bell, J. M., and Cameron, F. K., "Flow of Liquids Through Capillary Spaces", Journal of Physical Chemistry, 10: 658-74, 1905-06.

Berkman, Sophia, and Egloff, Gustav, Emulsions and Foams. New York: Reinhold Publishing Company, 1941. 591 pp.

Buckman, Schmitz and Gartner, "A Study of Certain Factors Influencing the Movement of Liquids in Wood", Journal of Physical Chemistry, 39: 102-20. 1935.

Burdon, R. S., Surface Tension and the Spreading of Liquids. London: Cambridge University Press, 1940. 85 pp.

Ceaglski, N. H., and Kiesling, F. C., "Capillary Flow in Porous Solids", Transaction of the American Institute of Chemical Engineers, 36: 211-25, 1940.

Clayton, William, The Theory of Emulsions and Their Technical Treatment. Third Edition; Philadelphia: P. Blakiston's Son and Company, Inc., 1938. 458 pp.

Dorsey, N. Ernest, "Measurement of Surface Tension", U. S. Bureau of Standards, Scientific Papers, 21, Bulletin Number 540, 575-95, 1926.

Du Nouy, P. Lecomte, Surface Equilibria of Colloids. New York: Chemical Catalog Company, Inc., 1926. 211 pp.

Ferguson, Allan, and Kennedy, S. J., "Notes on Surface Tension Measurements", Proceedings of the Physical Society, 44: 511-20, 1932.

Freundlich, Herbert, Colloid and Capillary Chemistry. Third Edition; London: Methuen and Company, Ltd., 1926. 883 pp.

International Society of Leather Trades' Chemists, Technical Aspects of Emulsions, New York: Chemical Publishing Company of New York, Inc., 1925. 150 pp.

International Society of Leather Trades' Chemists, Wetting and Detergency. New York: Chemical Publishing Company of New York, Inc., 1930. 208 pp.

Institute of Paper Chemistry, "Penetration of Papers by Liquids and Solutions", Paper Trades Journal, 110, No. 4, 44-50, 1940.

"Official Method for Determination of Wetting Power", Yearbook of the American Association of Textile Chemists and Colorists, 21: 199-206, 1944.

Rideal, Eric Keightley, "Flow of Liquids Under Capillary Pressure". The Philosophical Magazine and Journal of Science, 44: 1153-59, 1922.

Stamm, and Petering, "Treatment of Wood with Aqueous Solutions", Industrial Engineering Chemistry, 809-13, June, 1940.

"Surface Tension of Liquids", International Critical Tables, 4: 432-475.

Washburn, E. W., "The Dynamics of Capillary Flow," The Physical Review, 17: 273, 1921.

APPENDIX

APPENDIX

SAMPLE CALCULATIONS

1. Diameter of Capillary Tubing. The procedure to calculate the average diameter of capillary tubing was as follows: measured length of capillary was filled with mercury at a known temperature, the mercury in the capillary was then weighed and the tube diameter calculated.

Weight Hg = 0.7872 grams

Density Hg = 13.520 gms./cm^3

Length of Capillary = 50.8 cm.

Room Temperature = 30.6° C

$$\frac{0.7872 \times 100}{50.8 \times 13.5201} = 0.1146 \text{ mm}^2 \text{ (Capillary Area)}$$

$$\text{Area} = \tfrac{1}{4}\pi D^2 \quad \text{or} \quad D = 2\sqrt{\frac{A}{\pi}}$$

$$\text{Diameter of Capillary} = 2\sqrt{\frac{0.1146}{3.1416}} = 0.381 \text{ mm}$$

2. Conversion of Saybolt Universal Seconds to poises.

where μ = viscosity in poises

ρ = density in gms./cc.

t = time in seconds

then μ (28.2° C) = $(0.0022t - \frac{180}{t})$

$$\mu = 0.9600\ (0.0022 \times 36 - \frac{180}{36})$$

$$\mu = 0.02803 \text{ poises}$$

3. Rideal's Equation. Rideal obtained the following expression for the flow of a wetting liquid:

$$t = \frac{2\mu}{\sigma r} X^2 - \frac{\rho r^2}{8\mu} \log X + \frac{\rho^2 r^5}{512\mu^3 X^2}$$

Where: t = time in seconds

μ = viscosity in poises

σ = surface tension in dynes/cm.

r = the capillary radius in cm.

x = distance traveled by liquid in cm.

ρ = density of liquid in gm/cc.

Upon substitution of the values of the capillary radius 0.0354 and less the expression reduces to

$$t = \frac{2\mu}{\sigma r} X^2$$

as seen below at 29° C for 20 cm. penetration

$$t = \frac{2\,(0.0276)(20)^2}{33.82\,(0.0354)} - \frac{0.9590\,(0.0354)^2}{8\,(0.0276} + \frac{(0.9590)^2\,(0.0354)^5}{512\,(0.0276)^3\,(20)^2}$$

$$t = 18.4 - \underset{\text{negligible}}{0.0054} + \underset{\text{negligible}}{1.2 \times 10^{-8}}$$

4. Calculation of K in the Equation $t = K \mu/\sigma$ from Figure 7 for radius 0.0190.

$$\frac{1}{K} = \text{Slope} = \frac{y_1 - y_2}{x_1 - x_2}$$

$$\frac{1}{K} = \frac{2.35 \times 10^{-4} - 8.19 \times 10^{-4}}{22.4 - 75.2}$$

$$\frac{1}{K} = 1.105 \times 10^{-5}$$

$$K = 9.05 \times 10^{4}$$

Where K = slope

x & y = coordinates of curve

5. Effect of 0.25 centimeter head on horizontal capillary flow using Washburn's Equation at 29° C and radius 0.0354 centimeters.

$$x^2 = \frac{\sigma \cos\theta}{2\mu} rt + \frac{P t r^2}{4\mu}$$

$$x^2 = \frac{33.82}{2(0.02276)} (0.0354)\ 40.4 + \frac{(0.25)(980.6)(0.959)(40.4)(0.0354)^2}{4(0.02276)}$$

$$x^2 = 1055 + \frac{10}{} \text{ less than } 1\%$$

where x = distance in centimeters

σ = surface tension in dynes/cm

θ = angle of contact of liquid with surface

μ = viscosity in poises

r = capillary radius in centimeters

t = time in seconds

P = pressure due to head in dynes/cm^2

TABLE III

TIME OF CAPILLARY FLOW
VS.
CONCENTRATION AND TEMPERATURE

Time of Flow VS. Concentration

Concentration	Radius	Temperature °C	20 cm. time in seconds	40 cm. time in seconds
5%	.0354	29.0	12.0	35.8
10%	.0354	29.0	16.1	48.0
15%	.0354	29.0	26.0	77.4
20%	.0354	29.0	40.4	120.0
5%	.0190	29.0	22.4	66.7
10%	.0190	29.0	29.8	88.8
15%	.0190	29.0	48.4	144.0
20%	.0190	29.0	75.2	224.0

Time of Flow VS. Temperature

Temperature °C	Radius	Concentration	20 cm. time in seconds	40 cm. time in seconds
9.0	.0354	20%	59.6	178.0
16.0	.0354	20%	46.2	137.5
29.0	.0354	20%	40.0	119.0
32.8	.0354	20%	42.0	125.0
41.0	.0354	20%	43.5	129.5
9.0	.0190	20%	113.0	339.0
16.0	.0190	20%	90.0	269.0
31.0	.0190	20%	77.0	229.0
32.8	.0190	20%	80.2	238.0
41.0	.0190	20%	82.0	244.0

TABLE IV

VARIATION OF PHYSICAL PROPERTIES OF TEST EMULSION WITH TEMPERATURE

Density VS. Temperature °C

Temperature °C	Emulsion Concentration	Density in gm./cc
9.4	20%	0.9655
18.4	20%	0.9635
28.6	20%	0.9600
38.5	20%	0.9555
44.2	20%	0.9525

Viscosity VS. Temperature °C

Temperature °C	Emulsion Concentration	Viscosity in centipoises
8.4	20%	4.620
16.0	20%	3.3561
28.2	20%	2.803
36.0	20%	2.698
42.0	20%	2.652

Surface Tension VS. Temperature °C

Temperature °C	Emulsion Concentration	Surface Tension in cynes/cm.
9.0	20%	37.2
19.2	20%	35.6
28.6	20%	33.6
36.0	20%	31.3
42.0	20%	29.2

TABLE V

VARIATION OF PHYSICAL PROPERTIES OF TEST EMULSION WITH CONCENTRATION

Concentration	Surface Tension dynes/cm	Density cm/cc	Viscosity (centipoises)
5%	35.83	.9880	0.840
10%	34.87	.9782	1.125
15%	34.28	.9687	1.750
20%	33.82	.9590	2.776

Physical Properties at twenty nine degrees Centigrade

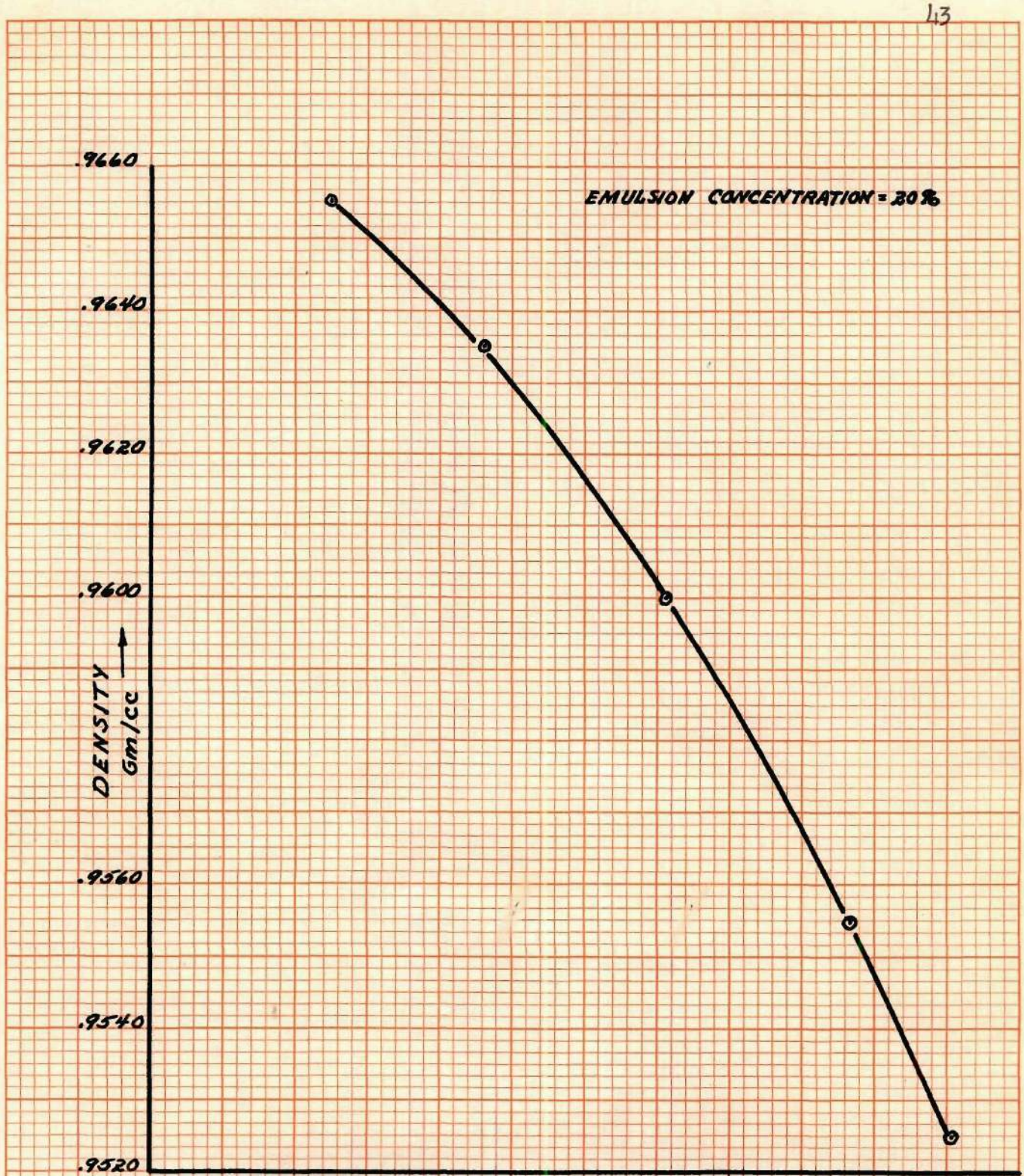

FIGURE 10

EMULSION DENSITY VS TEMPERATURE

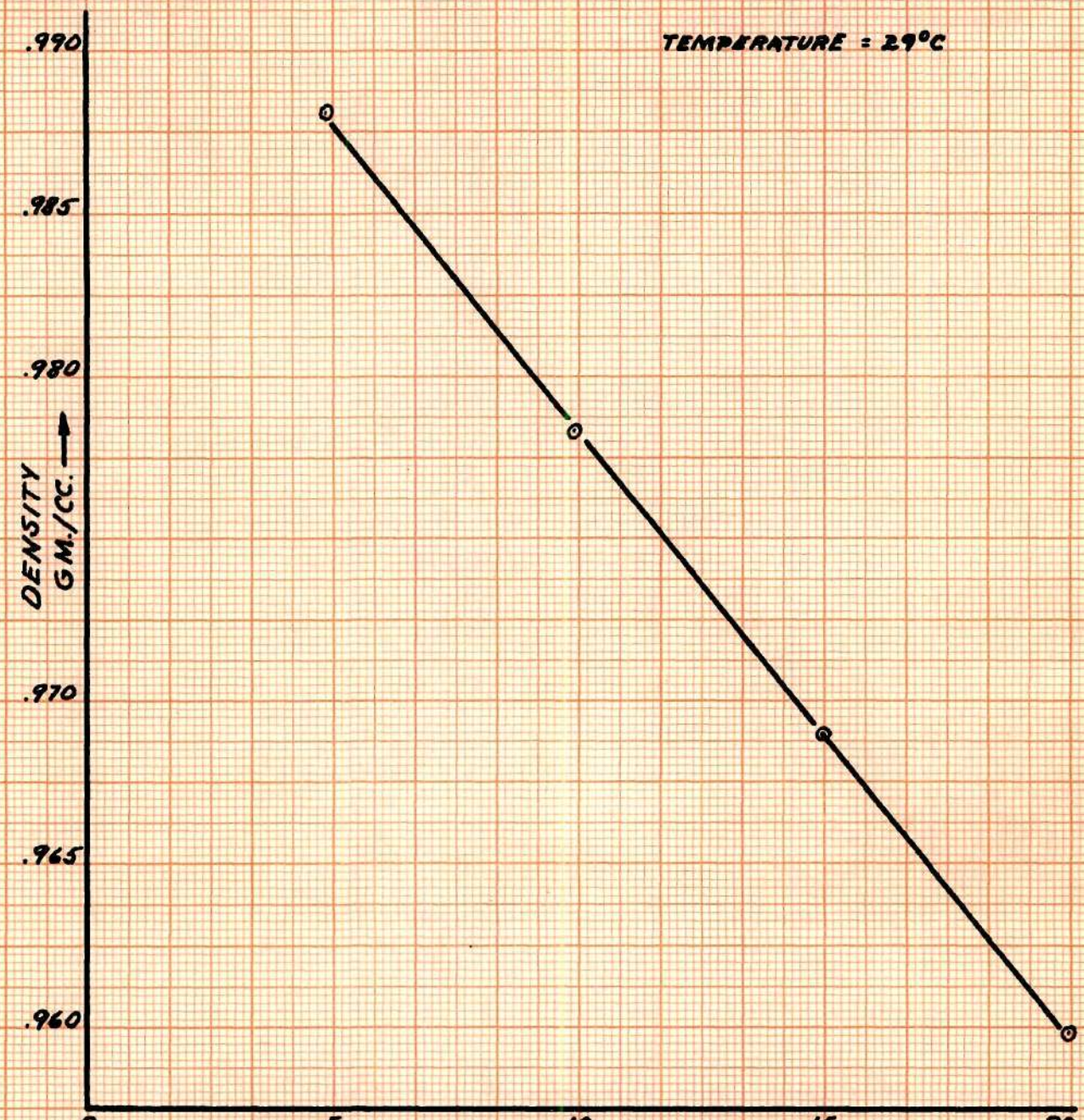

FIGURE 11

EMULSION DENSITY VS CONCENTRATION